Study on Al_2O_3 Extraction From Activated Coal Gangue under Different Calcination Atmospheres

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Coal gangue was calcinated under air, nitrogen, carbon dioxide, air–hydrogen, and hydrogen atmospheres. The effects of different calcination temperatures and atmospheres on the mineral composition of activated coal gangue were investigated by X-ray diffraction. Moreover, the acid leaching kinetics of aluminum oxide from coal gangue was investigated with sulfuric acid. It showed that the air atmosphere promoted kaolinite decomposition during coal gangue calcination. The hydrogen atmosphere promoted the activation and decomposition of kaolinite at reaction temperatures exceeding 650°C. The carbon dioxide atmosphere eliminated the influence of residual carbon on coal gangue. When the ratio of acid/coal gangue was 1.5 and reaction temperature was 650°C, the sulfuric acid leaching rate under air, air-hydrogen, carbon dioxide, hydrogen and nitrogen atmospheres were 93.66%, 90.90%, 84.06%, 81.91% and 77.54% respectively. The acid leaching reaction process conformed to unreacted shrinking core model of particle unchanged, and was controlled by the interfacial chemical reaction. The reaction kinetic equation for the leaching process was $1-(1-x)1/3=kt$ with an apparent activation energy of 48.97 kJ/mol.

Keywords: coal gangue, aluminum oxide, calcination and activation, atmosphere

Introduction

Years of exploitation and utilization have gradually reduced domestic high-quality bauxite resources. Therefore, it is increasingly difficult to meet the demands of the rapid development of aluminum-making industry in China. China relies on considerable quantities of imported bauxite, and is thus the highest bauxite importer in the world[1–2]. The coal gangue output of China is approximated at about 200 million tons per year. As of 2010, China has 5 billion tons of stockpiled coal gangue. The chemical components of coal gangue are SiO_2, Al_2O_3, and Fe_2O_3, which account for more than 80% of coal gangue, and Al_2O_3 accounting for 20% to 35%[3]. The effective extraction of Al_2O_3 from coal gangue will enable its high-value utilization and simultaneously ease the shortage of bauxite resources in China[4–5]. However, the current extraction rate of Al_2O_3 from coal gangue is low because the majority of Al_2O_3 in gangue exists as kaolinite, which is relatively stable and has low leaching activity. Research indicates that transforming stable kaolinite to metakaolin and further to an amorphous mineral might increase the leaching activity. Then, acid leaching or alkali leaching methods can effectively be used to ex-

tract Al_2O_3 from activated coal gangue[6]. Coal gangue activation methods include calcination activation, machinery activation, chemical activation and compound activation[7-13]. Calcination activation is a simple and convenient method to transform kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) to $Al_2O_3 \cdot 2SiO_2$, even amorphous SiO_2 and active Al_2O_3, these transformations increased the chemical reaction activity of coal gangue[14–16]. Previous research demonstrated that the calcination temperature and atmosphere were the two most important factors that affect coal gangue activity. Luo [17] posited that acid leaching to kaolinite rock calcinated at 750°C may increase the Al_2O_3 leaching rate. Wang [18] determined that a calcination temperature of 800°C effectively activates coal gangue. Si [19] demonstrated that the thermal conversion process of kaolinite is the same under N_2 and CO_2 atmospheres when the temperature is lower than 700°C. However, when the temperature exceeds 800°C, the CO_2 atmosphere suppresses kaolinite product transformation.

These studies show that different calcination temperatures and atmospheres have different effects on the activation of coal gangue. Therefore, the influence of calcination temperatures and atmospheres on coal gangue activation and subsequent acid leaching was systematically studied. Al_2O_3 extraction from activated coal gangue by acid leaching under air, nitrogen, hydrogen, air-hydrogen, carbon dioxide atmospheres at 500°C—950°C was investigated This work lays the foundation for the development and optimization of large-scale Al_2O_3 extraction from coal gangue by acid leaching.

Experiment

Samples

The coal gangue were collected from Sanjiaohe coal mine, in Shanxi Province, China, which is a black, gray, and massive rock with a hard texture and shell fracture.
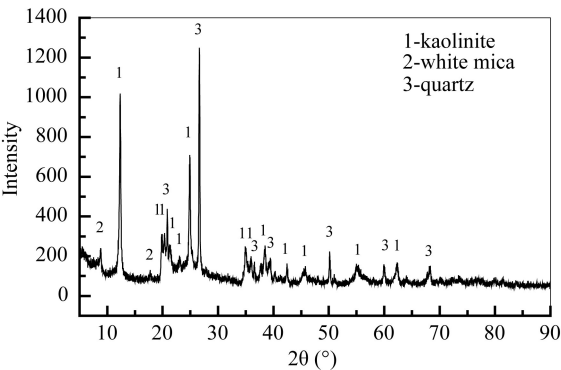

Fig. 1   X-ray infrared spectra of gangue

To obtain test samples, the coal gangue was crushed to less than 5 mm with a jaw crusher and then pulverized to less than 0.12 mm with a ball mill. The processed sam-

ples were dried at 105°C for 24 hours. Table 1 and Fig. 1 show the chemical and mineral composition of coal gangue, respectively. The coal gangue is composed of kaolinite, muscovite and quartz.

Table 1   The chemical composition of coal gangue   (%)

Component	SiO₂	Al₂O₃	Fe₂O₃	CaO
Content/% (Sanjiaohe)	43.44	26.87	4.24	1.96
Component	MgO	TiO₂	Loss on ignition	Totals
Content/% (Sanjiaohe)	0.44	0.09	22.05	99.09

Activation and acid leaching test

Calcination experiment

Calcination experiment was performed in a laboratory fixed bed reactor (Fig. 2). Prior to the experiment, 10 g of the coal gangue was spread evenly on a quartz tube reactor with quartz wool. The quartz tube was then fixed in the reaction device. The bottom of the reactor was connected to the air inlet and the top of the reactor was connected to the air outlet. In the calcination experiment, the gas cylinder was opened and the inlet gases was used with air, nitrogen, hydrogen, air–hydrogen, and carbon dioxide respectively. The gas flow rate was set to 50 ml/min. The air atmosphere was adjusted with a nitrogen flow rate of 40 ml/min and an oxygen flow rate of 10 ml/min. The air–hydrogen atmosphere was adjusted with a nitrogen flow rate of 25 ml/min, an oxygen flow rate of 5 ml/min and a hydrogen flow rate of 25ml/min. The final temperatures were 500°C, 650°C, 800°C, and 950°C. The residence time was 2 h. The sample was left in the reactor for calcination and then cooled to room temperature. Finally, the sample was removed, weighed, and placed in the dryer.
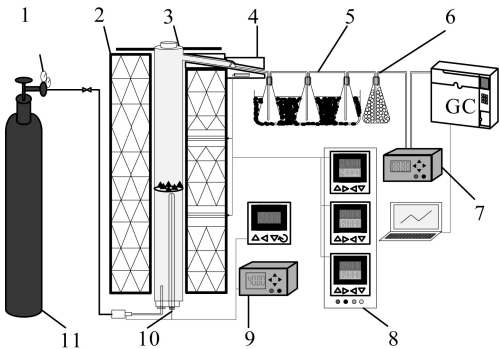

1. pressure relief valve, 2. Furnace, 3. Reactor, 4. heating jacket, 5. Condensation, 6. Dryer, 7. flow meter, 8. temperature controller, 9. flow control, 10. Thermocouple, 11. gas cylinders

Fig. 2   Schematic diagram of the fixed-bed reactor

Acid leaching experiment

Al$_2$O$_3$ was extracted from calcinated coal gangue via sulfuric acid leaching. The required amount of concentrated sulfuric acid was measured with a graduated cylinder and placed in a 200-mL breaker, which was then placed on a magnetic heating stirrer. The calcinated coal gangue were added and stirred at a constant temperature of 100°C for 1.5h and then vacuum-filtered after the reaction was completed. The filtrate was transferred to a 100-mL graduated cylinder to be measured and recorded. The composition of the filtrate was analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES).

The leaching rate ηA of aluminum oxide in coal gangue was calculated according to the formula (1):

$$\eta_A = \frac{T_{A1} - M_{A1}}{T_{A1}} \times 100\% \qquad (1)$$

$$M_{A1} = C_{A1} \times V \qquad (2)$$

where T_{Al} is the amount of aluminum oxide in the coal gangue (g), M_{Al} is the amount of aluminum oxide in the acid leachate (g), C_{Al} is the concentration of acid leachate (g/mL), and V is the volume (mL) of the acid leachate.

Test and analysis of the samples

XRD analysis was performed with a D8 Focus X-ray diffractometer (Bruker Company, Germany) to investigate mineral composition present in the samples. The target was Cu, tube current was 40 mA, tube voltage was 40 kV, scanning range was 2θ = 5°–90°, scanning speed was 0.06 s/step, and step interval was 0.02°/step. XRD analysis was performed with X'Pert–High score software and PDF2003 database.

Result and discussions

Activation mechanism of coal gangue calcinated at different atmospheres

Fig. 3 shows the XRD analysis of coal gangue that were calcinated and activated under different atmospheres and temperatures. Calcination temperature was the main factor that affected coal gangue activation and kaolinite transformation. The diffraction peak of kaolinite decreased with the increase of the calcination temperatures[13]. Fig. 3 shows that when the calcination temperature reached 500°C, the main components of coal gangue were kaolinite, quartz, and muscovite under different atmosphere. However, the diffraction peaks of kaolinite and muscovite weakened because of the decomposition of kaolinite and muscovite[16]. When the calcination temperature reached 650°C, the kaolinite diffraction peak further weakened and disappeared, which indicated that large quantities of hydroxyl radicals in the kaolinite and muscovite minerals of the coal gangue were decomposed

and were released. The structure of the crystal phase in coal gangue changed, and kaolinite (Al$_2$O$_3$·2SiO$_2$·2H$_2$O) gradually transformed into metakaolin (Al$_2$O$_3$·2SiO$_2$)[14].

The kaolinite diffraction peak disappeared as the calcination temperature increased, which resulted from the complete destruction of kaolinite structure. Fig. 3 shows that the crystal structure of quartz did not change significantly, which indicated its stability during the coal gangue calcination.
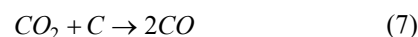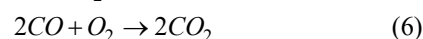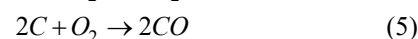
To quantify the effects of different temperatures and atmospheres on the decomposition and transformation of kaolinite in coal gangue, the decomposition rate of kaolinite was proposed and obtained by the change in the intensity of (001) peak of kaolinite relative to the strongest peak (101) of quartz at 650°C under different atmospheres:

$$\alpha = 1 - \frac{\left(I_k / I_Q\right)_{\text{calcined}}}{\left(I_K / I_Q\right)_{\text{raw}}} \qquad (3)$$

where I_k and I_Q represent the intensity of the diffraction peak of kaolinite (001) and the diffraction peak of quartz (101), respectively. The decomposition rates of kaolinite in coal gangue calcinated at 650°C were 52.44%, 50.90%, 47.04%, 45.36%, and 43.42% under air, air-hydrogen, carbon dioxide, hydrogen, and nitrogen atmospheres, respectively.

Effects of calcination atmosphere on coal gangue activity

Comparing the effects of different atmospheres on calcination activation showed that the diffraction peak intensity of kaolinite was the most obvious under the air atmosphere because the heat from carbonaceous combustion promoted the decomposition and transformation of kaolinite in coal gangue. O$_2$ in the air reacted with the carbon in coal gangue, which generated CO or CO$_2$. CO further reacted with O$_2$ to generate CO$_2$, which diffused to the particle surface and reacted with carbon to generate CO. The possible reaction pathways are as follows:

$$C + O_2 \rightarrow CO_2 \qquad (4)$$

$$2C + O_2 \rightarrow 2CO \qquad (5)$$

$$2CO + O_2 \rightarrow 2CO_2 \qquad (6)$$

$$CO_2 + C \rightarrow 2CO \qquad (7)$$

Li [20] studied the effect of kaolinite on coal combustion and found that when coal gangue was calcinated under an air atmosphere, the combustion of the carbon in the coal gangue promoted the calcination and transformation of kaolinite. Under N$_2$ atmosphere and increasing temperature, carbonaceous substances may escape by devolatilization from the coal gangue. However, the peak changes in the XRD spectrum indicated that the decomposition rate under the N$_2$ atmosphere was slower than that under the air atmosphere. This indicated that the

main reaction was the hydroxyl-free reaction of kaolinite under the nitrogen atmosphere. As calcination temperature increased, the stable alumina-oxygen octahedron in kaolinite was gradually destroyed, and as the alumina-oxygen bond and silicon-oxygen bonds were weakened, kaolinite gradually transformed into metakaolin and released water. The carbon in coal gangue under N_2 atmosphere could not combust as that under air atmosphere, kaolinite decomposition was relatively slower. Therefore, the following reaction occurred under N_2 atmosphere:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \quad (8)$$

Under the hydrogen atmosphere, the changes in the diffraction peaks of kaolinite were similar to those under the nitrogen atmosphere. However, when calcination temperature exceeded 650°C, the kaolinite diffraction peaks significantly decreased in comparison with those under other atmospheres. This behavior indicated that hydrogen atmosphere promoted the transformation of kaolinite and the activation of coal gangue at higher temperatures.

Comparing the samples calcinated under the carbon dioxide atmosphere with the original samples, it showed that the kaolinite diffraction peaks at 650°C and 800°C did not decrease significantly because carbon preferentially reacted with CO_2 in the coal gangue under CO_2 atmosphere instead of with aluminum silicate [21–22]. Therefore, the kaolinite decomposition rate under the CO_2 atmosphere was low. CO_2 first diffused through the ash layer to the surface of the unreacted kaolinite particles and reacted with the carbon in kaolinite, which generated CO and spread outwards:

$$CO_2 + C \rightarrow 2CO \quad (9)$$

Effects of calcination of coal gangue on acid leaching

The acid leaching test was performed under different conditions and the results are shown in Fig. 4. When the calcination temperatures increased from 500°C to 650°C, the leaching rate of calcinated coal gangue increased gradually and reached a maximum value at 650°C. The acid leaching rate decreased when the calcination temperatures exceeded 650°C. The results in Fig. 4 show that the acid leaching rates of calcinated coal gangue at 650°C were 93.66% under the air atmosphere, 90.90% under air–hydrogen atmosphere, 84.06% under carbon dioxide atmosphere, 81.91% under hydrogen atmosphere, and 77.54% under nitrogen atmosphere. These results are consistent with the change in the decomposition and transformation rates of kaolinite during the calcination of the coal gangue.

Sulfuric acid leaching rates of calcinated coal gangue under air and air-hydrogen atmospheres were higher than those under the other atmospheres, which showed that an oxidizing atmosphere promoted carbon in coal gangue combustion and kaolinite decomposition, as well as accelerated metakoalin transformation[15]. When coal gangue calcinated under the nitrogen (inert gas) atmosphere, the carbonaceous substances only pyrolysis to form semi-coke, which likely increased the resisitance of mass transfer and solid-liquid separation resistance in the acid leaching reaction, thus decreasing acid leaching rate[16].

The effect of low calcination temperature on the leaching rate of alumina in the calcinated coal gangue was not obvious under the hydrogen atmosphere (reducing atmosphere). As the temperature increase, the leach-
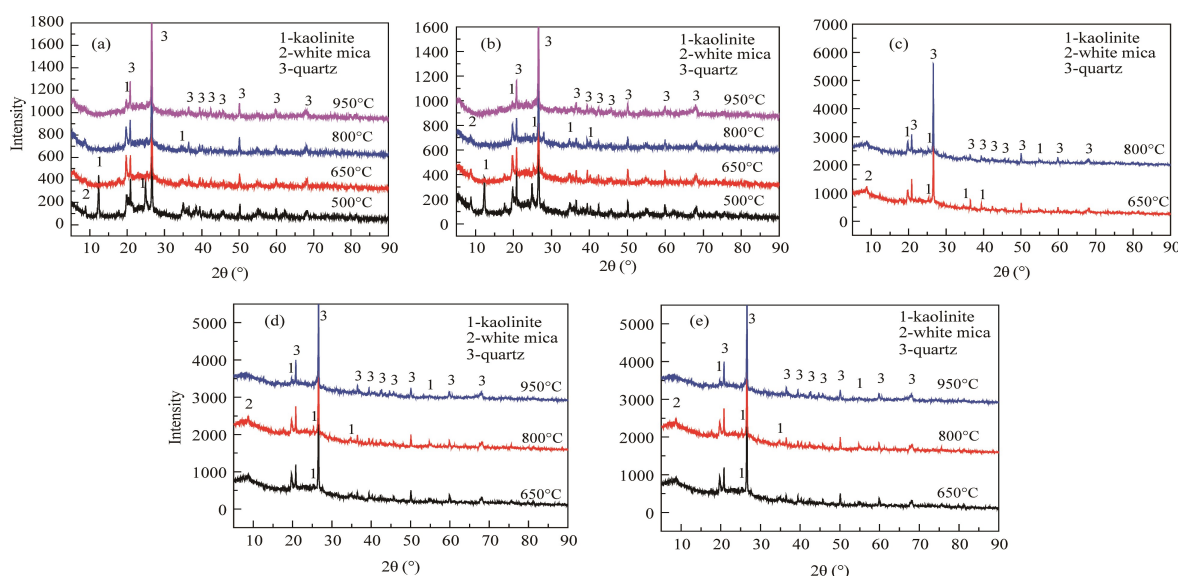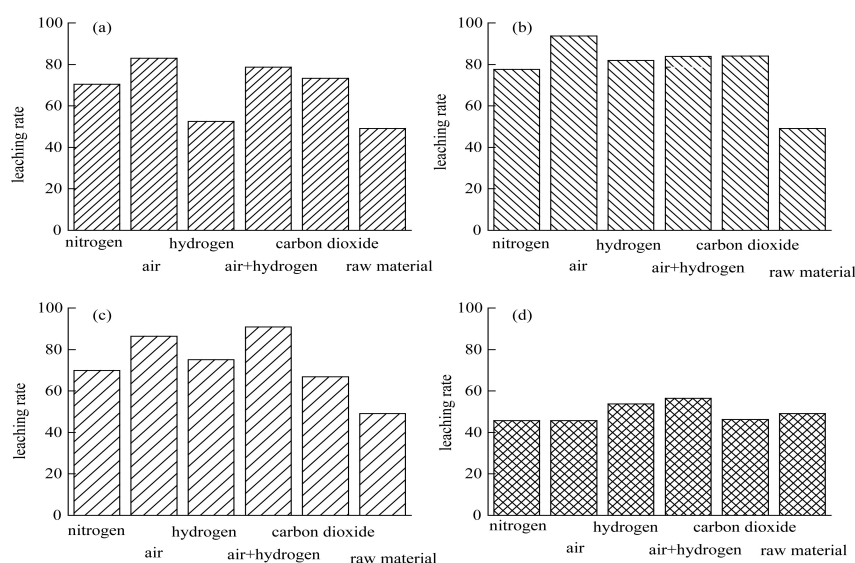

Fig. 3   X-ray diffraction spectrum of activated coal gangue in different atmosphere (a-nitrogen, b-air, c-nitrogen+hydrogen, d-hydrogen, e-carbon dioxide)

Fig. 4 The leaching rate of activated coal gangue under different atmospheres and temperature (a. 500°C, b. 650°C, c. 800°C, d. 950°C)

ing rate under this atmosphere was higher than that under the other atmospheres because hydrogen produced a reduction reaction that destroyed the oxide structure of some minerals to promote the transformation from a stable structure into a non-stable structure[17].

At 650°C, the leaching rate under the air-hydrogen atmosphere was slightly higher than those under the nitrogen and hydrogen atmosphere. Furthermore, the leaching rate under the air–hydrogen atmosphere was higher than the other atmosphere when the calcination temperature was above 800°C, which showed that hydrogen calcination promoted coal gangue activation at higher temperature.

The leaching rate of coal gangue under carbon dioxide atmosphere was 84.06% when calcined at 650°C, and the acid leaching rate of the calcinated coal gangue was higher than that under the nitrogen atmosphere, which showed that the CO_2 atmosphere eliminated the influence of carbonaceous substances in coal gangue. However, the local reaction temperature may decrease because the reduction reaction of CO_2 and carbon is an endothermic reaction. The decrease in temperature may partially affect the acid leaching reaction and the acid leaching rate.

Reaction kinetics of alumina extraction during coal gangue acid-leaching

The reaction of kaolinite in the coal gangue and sulfuric acid can generate SiO_2, H_2O, and $AlH(SO_4)_2$. Meanwhile $CaCO_3$ in the coal gangue react with sulfuric acid to generate H_2O, CO_2, and $Ca(SO_4)_2$[19]. The influence of acid leaching time on the leaching rate of aluminum from coal gangue was analyzed. Here, the leaching time was 0.5, 1, 1.5, and 2 h respectively. The chemical reaction of coal gangue follows the shrinking core model with surface reaction control, and the dynamic equation

of coal gangue reaction can be described as[23]:

$$1-\left(1-X\right)^{1/3} = t / t_f \tag{10}$$

where X indicates the reactant conversion rate, t indicates the reaction time, and t_f indicates the complete reaction time.

$$t_f = \rho_B R_s / B m_B k C \tag{11}$$

where ρ_B is the solid reactant concentration, Rs is the solid particle initial radius, B is the measure coefficient of the solid reactant, m_B is the molecular weight of the solid reactant, k is the reaction rate constant, and C is the liquid reactant concentration.

For a fixed solid-liquid phase reaction, t_f is considered as a constant. Thus, the formula can be converted to:

$$1-\left(1-X\right)^{1/3} = kt \tag{12}$$

The relationship between sulfuric acid leaching rate and reaction time at different calcination temperatures are shown in Fig. 5.
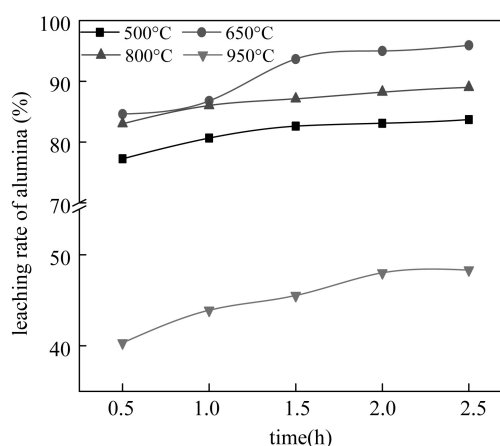
Fig. 5 Relationship between leaching rate of alumina and reaction time at different temperatures

Fig. 6 presents the curve fitting results of $1-(1-x)^{1/3}$ and reaction time t. The fitting correlation coefficient at 500°C, 650°C, 800°C, and 950°C were 0.9963, 0.9923, 0.9971, and 0.9961, respectively. The apparent rate constant K was calculated from Fig. 6 and were 0.04772, 0.06679, 0.05472, and 0.02348 h^{-1}.
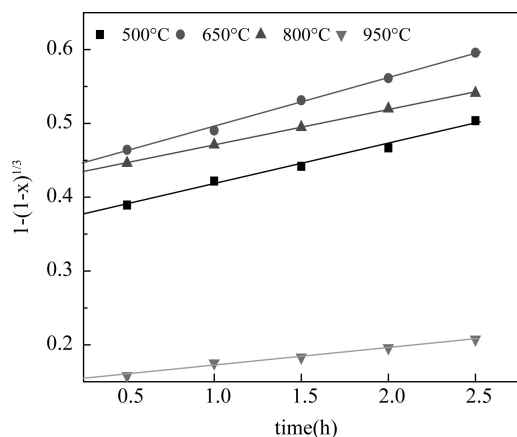
Fig. 6   Relationship between $1-(1-x)^{1/3}$ and reaction time at different temperatures

The K values calculated in Fig. 7 were substituted into the Arrhenius equation, $k = Ae^{-E_a/RT}$, which was then integrated on both sides of the equation $\ln k = \ln A - \dfrac{-E_a}{RT}$. Linear regression of T^{-1} was then calculated by lnk, and the results are shown in Fig. 7. Therefore, the apparent activation energy of the acid leaching reaction was 48.97 kJ/mol.
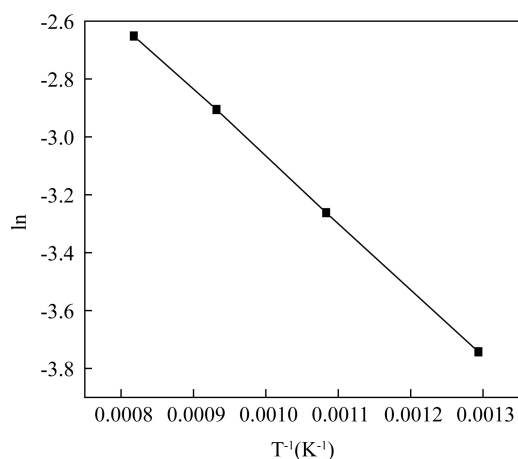
Fig. 7   Arrhenius diagram

Conclusion

Acid leaching method for extracting Al₂O₃ from coal gangue was discussed. Moreover, the effects of calcina-tion atmosphere and temperature on Al₂O₃ leaching rates in coal gangue were investigated. Based on the results above mentioned, the following conclusions can be obtained:

(1) Air atmosphere has a preferable activation effect because carbon combustion in the coal gangue promoted the transformation of kaolinite to metakaolin. The effect of hydrogen atmospheres was mainly in high temperature condition. Carbon preferentially reacted with CO₂, but not with aluminum under the CO₂ atmosphere.

(2) When coal gangue was calcinated at 650°C under air, air–hydrogen, carbon dioxide, hydrogen, or nitrogen atmospheres, the decomposition rates of kaolinite were 52.44%, 50.90%, 47.04%, 45.36%, and 43.42%, respectively. The acid leaching rate of coal gangue calcinated under different atmospheres were 93.66% under the air atmosphere, 90.90% under the air–hydrogen mixed atmosphere, 84.06% under the carbon dioxide atmosphere, 81.91% under the hydrogen atmosphere, and 77.54 % under the nitrogen atmosphere.

(3) Under the conditions of reaction temperatures 600°C–950°C, the sulfuric acid leaching of coal gangue conformed to unreacted shrinking core model. The reaction kinetics equation of the process was $1-(1-x)^{1/3} = kt$ with an apparent activation energy of 48.97 kJ/mol.

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